JC20 Rec'd PCT/PTO 1 8 MAR 2002

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| DESIGNATED/ELECTED OFFICE (DO/EO/US) | | | | | | |
| CONCERNING A FILING UN | | | | | | |
| ATTORNEY DOCKET NUMBER IN-12122 | U.S. APPLICATION NO (IF KNOWN SEE 37 RR 15) | | | | | |
| INTERNATIONAL APPLICATION NO. | INTERNATIONAL FILING DATE | PRIORITY DATE CLAIMED | | | | |
| PCT/EP 00/08640 | 05.09.00 | 17.09.99 | | | | |
| PREPARATION OF FLEXIBLE SLA | ABSTOCK FOAM POLYOLS | | | | | |
| Georg Heinrich GROSCH; Harald | LARBIG; Reinhard LORENZ; Dieter JU | NGE; and Kathrin HARRE. | | | | |
| Applicant herewith submits to the United Sta | tes Designated/Elected Office (DO/EO/US) the folions concerning a filing under 35 U.S.C. 371. | | | | | |
| 2. This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. | | | | | | |
| This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371 (b) and PCT Articles 22 and 39(1). A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date | | | | | | |
| 5. X A copy of the International Application as filed (35 U.S.C. 371(c)(2)) a. X are transmitted herewith (required only if not transmittal by the International Bureau). b. have been transmitted by the International Bureau. c. is not required, as the application was filed in the United States Receiving Office (RO/US) 6. X A translation of the International Application into English (35 U.S.C. 371(C)(2)). | | | | | | |
| a. | International Application under PCT Article 19 (35 rewith (required only if not transmitted by the Internated by the International Bureau. de; however, the time limit for making such amendred and will not be made to the claims under PCT Article 19 (35 U.S.C. 371). | ational Bureau). nents has NOT expired. | | | | |
| 9. X An oath or declaration of the inve | entor(s) (35 U.S.C. 371(c)(4)). | | | | | |
| Items 11. to 16. below concern other docu | International Preliminary Examination Report unde ment(s) or information included: ment under 37 CFR 1.97 and 1.98. | r PCT Article 36 | | | | |
| 12. X An assignment document for rec | cording. A separate cover sheet in compliance with | n 37 CFR 3.28 and 3.31 is included | | | | |
| | oreliminary amendment. and/or address letter. card om the PCT Published Application of a Change (Form PCT/1B/306) andence is being ice in an envelope | | | | | |
| No.EL 900586466 US addressed to the Assistor Patents, Washington, D.C. 20231 | stant Commissioner | | | | | |
| on MARCH 18 2002. | | | | | | |

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| U.S. APPLICATION NO. | 188225 lf | NTERNATIONAL APPLICAT PCT/EP 00/08640 | TON NO. | ATTORNEY'S DO IN-12122 | CKET NUMBER | |
| | ing fees are submitted | | | CALCULATION | S PTO USE ONLY | |
| Basic National Fee (3 | 7 CFR 1.492(a)(1)-(5)): | | | | | |
| | | EPO or JPO | | ! | | |
| | | to USPTO (37 CFR 1.48 | | | | |
| No international prelim | inary examination fee pa | aid to USPTO (37 CFR 1 | .482) | | | |
| but international search | n ree paid to USPTO (3) | 7 CFR 1.445(a)(2)) | \$740.00 | | | |
| Neither international printernational search fe | reliminary examination foe e (37 CFR 1.445(a)(2)) p | ee (37 CFR 1.482) nor paid to USPTO | \$1,040.00 | | | |
| International preliminal and all claims satisfied | ry examination fee paid provisions of PCT Artic | to USPTO (37 CFR 1.482 le 33(2)-(4) | 2) \$100.00 | | | |
| | ENTER APPROP | RIATE BASIC FEE | AMOUNT = | \$890.00 | | |
| Surcharge of \$130.00 to months from the earlies | for furnishing the oath or st claimed priority date (| r declaration later than [37 CFR 1.492(e)). |] 20 [X] 30 | \$ | | |
| Claims | Number Filed | Number Extra | Rate | | | |
| Total Claims | 14 - 20 = | 0 | X \$18.00 | \$0.00 | <u> </u> | |
| Independent claims | 3 - 03 = | 0 | X \$84.00 | \$0.00 | | |
| Multiple dependent claims | \$280.00 | | | | | |
| | \$1170.00 | | | | | |
| TOTAL OF ABOVE CALCULATION = Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28). | | | | \$ | | |
| SUBTOTAL = | | | \$1170.00 | | | |
| Processing fee of \$130 months from the earlies | .00 for furnishing the Enst claimed priority date (| nglish translation later the 37 CFR 1.492(f)). | [] 20 [] 30 + | \$ | | |
| | | TOTAL NA | TIONAL FEE = | \$1170.00 | | |
| Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be | | | \$40.00 | | | |
| accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property + | | | | £4040.00 | | |
| TOTAL FEES ENCLOSED = | | | \$1210.00 | | | |
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| | | | | Charged | \$1210.00 | |
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- X Please charge my Deposit Account No. 23-3425 in the amount of \$1210.00 to cover the above fees A triplicate copy of this sheet is enclosed.
- X The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 23-3425. A triplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status

SEND ALL CORRESPONDENCE TO:

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34,789

REGISTRATION NUMBER

JC13 Rec'd PCT/PTO 1 8 MAR 2002

PATENT

(Docket No. 12122)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of

GEORG HEINRICH GROSCH ET AL.

Serial No.: NEW

Filed: HEREWITH

For: "PREPARATION OF FLEXIBLE

SLABSTOCK FOAM POLYOLS"

Group Art Unit: NEW

Examiner: NEW

I hereby certify that the attached correspondence is being deposited with the United States Postal Service in an envelope as "Express Mail Post Office to Addressee" addressed to Box Patent Applications, Assistant Commissioner of Patents, Washington, D.C. 20231, on March 18, 2002.

Express Mail No. EL 900586466 US

PRELIMINARY AMENDMENT

BOX PCT APPLICATIONS

Assistant Commissioner of Patents Washington, D.C. 20231

Sir:

In reference to the above-referenced patent application, please enter the following amendment and consider the accompanying remarks prior to examination thereof on the merits.

IN THE CLAIMS:

Please amend the claims as follows:

1. (amended) A polyether alcohol prepared by ring-opening polymerization of ethylene oxide and at least one alkylene oxide having at least three carbon atoms in the molecule onto H-functional initiator substances, wherein ethylene oxide or a mixture of ethylene oxide and at least one alkylene oxide having at least three carbon atoms in the molecule, where the mixture has an

ethylene oxide content of at least 98% by weight, based on the mixture, is added, in each case in an amount of not more than 40% by weight, based on the weight of the polyether alcohol, onto the initiator substance and subsequently at least one alkylene oxide having at least three carbon atoms in the molecule or a mixture of ethylene oxide and at least one alkylene oxide having at least three carbon atoms in the molecule, where the mixture has a maximum ethylene oxide content of 20% by weight, based on the mixture, is added on, and at least one multimetal cyanide compound is used as a catalyst.

- 2. (amended) A polyether alcohol as claimed in claim 1, wherein the alkylene oxides having at least three carbon atoms in the molecule are propylene oxide, butylene oxide, isobutylene oxide or any mixtures of at least two of the alkylene oxides.
- 8. (amended) A polyether alcohol as claimed in claim 4, wherein at least one basic compound is used as catalyst for the addition of the ethylene oxide or of the mixture of ethylene oxide and at least one alkylene oxide having at least 3 carbon atoms in the molecule, where the mixture has an ethylene oxide content of at least 98% by weight, based on the mixture, onto the initiator substance and at least one multimetal cyanide compound is used as catalyst for adding on the alkylene oxide or oxides having at least 3 carbon atoms in the molecule or the mixture of ethylene oxide and at least one alkylene oxide having at least 3 carbon atoms in the molecule, where the mixture has a maximum ethylene oxide content of 20% by weight, based on the mixture, and at least one basic compound is used as catalyst for adding on the ethylene oxide at the end of the chain.
- 9. (amended) A polyurethane produced by reacting polyisocyanates with compounds having at least two hydrogen atoms which are reactive toward isocyanate groups, wherein a polyether

alcohol as claimed in any of claims 1 to 5 is used as compound having at least two hydrogen atoms which are reactive toward isocyanate groups.

Please add the following new claim:

- 10. (new) A polyether alcohol prepared by ring-opening polymerization of ethylene oxide and at least one alkylene oxide having at least three carbon atoms in the molecule onto H-functional initiator substances wherein
 - a1) ethylene oxide

or

a2) a mixture of ethylene oxide and at least one alkylene oxide having at least three carbon atoms in the molecule, where the mixture has an ethylene oxide content of at least 98% by weight, based on the mixture,

is added in an amount of not more than 40% by weight based on the weight of the polyether alcohol onto the initiator substance and subsequently

- b1) at least one alkylene oxide having at least three carbon atoms in the molecule or
 - b2) a mixture of ethylene oxide and at least one alkylene oxide having at least three carbon atoms in the molecule, where the mixture has a maximum ethylene oxide content of 20% by weight, based on the mixture,

is added in the presence of at least one multimetal cyanide compound catalyst.

Appendix A

- 1. (amended) A polyether alcohol [which can be] prepared by ring-opening polymerization of ethylene oxide and at least one alkylene oxide having at least three carbon atoms in the molecule onto H-functional initiator substances, wherein ethylene oxide or a mixture of ethylene oxide and at least one alkylene oxide having at least three carbon atoms in the molecule, where the mixture has an ethylene oxide content of at least 98% by weight, based on the mixture, is added, in each case in an amount of not more than 40% by weight, based on the weight of the polyether alcohol, onto the initiator substance and subsequently at least one alkylene oxide having at least three carbon atoms in the molecule or a mixture of ethylene oxide and at least one alkylene oxide having at least three carbon atoms in the molecule, where the mixture has a maximum ethylene oxide content of 20% by weight, based on the mixture, is added on, and at least one multimetal cyanide compound is used as a catalyst.
- 2. (amended) A polyether alcohol as claimed in claim 1, wherein the alkylene oxides having at least three carbon atoms in the molecule are propylene oxide, butylene oxide, isobutylene oxide or any mixtures of at least two of the alkylene oxides [mentioned are used as alkylene oxides having at least three carbon atoms in the molecule].
- 8. (amended) A [process for preparing] polyether alcohol[s] as claimed in claim 4, wherein at least one basic compound is used as catalyst for the addition of the ethylene oxide or of the mixture of ethylene oxide and at least one alkylene oxide having at least 3 carbon atoms in the molecule, where the mixture has an ethylene oxide content of at least 98% by weight, based on the mixture, onto the initiator substance and at least one multimetal cyanide compound is used as catalyst for adding on the alkylene oxide or oxides having at least 3 carbon atoms in the molecule or the mixture of ethylene oxide and at least one alkylene oxide having at least 3 carbon atoms in

the molecule, where the mixture has a maximum ethylene oxide content of 20% by weight, based on the mixture, and at least one basic compound is used as catalyst for adding on the ethylene oxide at the end of the chain.

9. (amended) A polyurethane [which can be] produced by reacting polyisocyanates with compounds having at least two hydrogen atoms which are reactive toward isocyanate groups, wherein a polyether alcohol as claimed in any of claims 1 to 5 is used as compound having at least two hydrogen atoms which are reactive toward isocyanate groups.

REMARKS

Applicants respectfully request examination of the present application as amended herein. Claims 1-9 are pending in this application, an amended sheet of claims having been filed in the PCT application, a copy of the amended sheet in English and German accompanies this filing of the national phase application. Upon entry of the above preliminary amendment, claims 1-10 remain pending in the application. Claims 1, 2, 8 and 9 have been amended. New claim 10 has been added.

A marked-up version of the amended claims is attached hereto in Appendix A. Should the Examiner have any questions, please contact the undersigned attorney.

Respectfully submitted,

Date: 3/15/02

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Mary K. Cameron

Attorney for Applicants Registration No. 34,789

JC13 Rec'd PCT/PTO 1 8 MAR 2002

Preparation of flexible slabstock foam polyols

The present invention relates to a process for preparing 5 polyether alcohols, to the polyether alcohols prepared by this process and to their use for producing polyurethanes.

Polyether alcohols are used in large quantities for producing polyurethanes. They are usually prepared by catalytic addition of 10 lower alkylene oxides, in particular ethylene oxide and propylene oxide, onto H-functional initiator substances. Catalysts used are usually basic metal hydroxides or salts, with potassium hydroxide having the greatest practical importance.

15 The alkylene oxides are usually added on as a block or as a random mixture. In the blockwise molecular addition, only one alkylene oxide at a time is added on, while in the random molecular addition, a mixture of alkylene oxides is present in the reaction mixture.

20

In the industry, ethylene oxide and propylene oxide are usually used as alkylene oxides, since they are readily available and inexpensive. The reactivity of ethylene oxide is higher than that of propylene oxide, so that the molecular addition of ethylene 25 oxide proceeds at a higher reaction rate. To increase the space-time yield in the preparation of polyether alcohols it would be desirable for the proportion of ethylene oxide in the polyether alcohol to be as high as possible. Provision of polyether alcohols which are intended for use in flexible foams 30 with terminal ethylene oxide blocks is known and customary. The associated increase in the number of primary hydroxyl groups in the polyether alcohols results in an increase in their reactivity in the reaction with polyisocyanates. However, the increase in the ethylene oxide content of the polyether alcohol also results 35 in an increase in the hydrophilicity of the polyether alcohol, which can lead, inter alia, to undesirable gel formation in the polyether alcohols.

Furthermore, in the synthesis of polyether alcohols having long 40 chains, as are used for producing flexible polyurethane foams, increasing chain growth is associated with secondary reactions which lead to defects in the chain structure. These by-products are referred to as unsaturated constituents and lead to a deterioration in the properties of the resulting polyurethanes.

45 Many attempts have therefore been made in the past to prepare polyether alcohols having a low content of unsaturated constituents. In particular, the alkoxylation catalysts used have

been altered in a targeted way in an attempt to achieve this. Thus, EP-A-268 922 proposes using cesium hydroxide. Although this enables the content of unsaturated constituents to be reduced, cesium hydroxide is expensive and disposing of it is 5 problematical.

Furthermore, the use of multimetal cyanide complexes, usually zinc hexacyanometalates, also known as DMC catalysts, for preparing polyether alcohols having low contents of unsaturated 10 constituents is also known. There is a large number of documents in which the preparation of such compounds is described. Thus, DD-A-203 735 and DD-A-203 734 describe the preparation of polyetherols using zinc hexacyanocobaltate.

The preparation of the zinc hexacyanometalates is also known. These catalysts are usually prepared by reacting solutions of metal salts such as zinc chloride with solutions of alkali metal or alkaline earth metal cyanometalates, e.g. potassium hexacyanocobaltate. A water-miscible, heteroatom-containing component is generally added to the resulting suspension immediately after the precipitation step. This component can also be present initially in one or both starting solutions. This water-miscible, heteroatom-containing component can be, for example, an ether, polyether, alcohol, ketone or a mixture
25 thereof. Such processes are described, for example, in US 3,278,457, US 3,278,458, US 3,278,459, US 3,427,256, US 3,427,334, US 3,404,109.

Polyether alcohols used for producing flexible slabstock foams generally have a complete propylene oxide inner block which can make up as much as 40% by weight of the total polyol bound directly to the initiator substance and on this propylene oxide inner block have mixed blocks of propylene oxide and ethylene oxide which make up at least 60% by weight of the total polyol and contain at least 2% by weight of ethylene oxide. These polyols are generally prepared using basic catalysts.

WO-A-97/27,236 describes the preparation of a flexible slabstock foam polyol in which at least one propylene oxide inner block is added on using multimetal cyanides as catalyst. However, this process does not permit a further increase in the ethylene oxide content of the polyether alcohol without the abovementioned disadvantages.

It is an object of the present invention to develop polyether alcohols which have a high ethylene oxide content without there being a significant increase in the hydrophilicity of the product.

We have found that this object is achieved by a polyether alcohol which can be prepared by ring-opening polymerization of ethylene oxide and alkylene oxides having at least 3 carbon atoms, which comprises an inner block of ethylene oxide or a mixture of ethylene oxide and alkylene oxides having at least 3 carbon atoms, and attached to this a block comprising at least one alkylene oxide having at least 3 carbon atoms or a mixture of ethylene oxide and alkylene oxides having at least 3 carbon atoms, preferably propylene oxide, where the mixed blocks

15 preferably contain at least 2% by weight and not more than 20% by weight of ethylene oxide, based on the mixture.

The present invention accordingly provides polyether alcohols which can be prepared by ring-opening polymerization of ethylene oxide and propylene oxide onto H-functional initiator substances, wherein not more than 40% by weight, based on the weight of the polyether alcohol, of ethylene oxide or a mixture of ethylene oxide and alkylene oxides having at least 3 carbon atoms, where the mixture has an ethylene oxide content of at least 98% by weight, based on the mixture, is added onto the initiator substance and subsequently at least one alkylene oxide having at least 3 carbon atoms or a mixture of ethylene oxide and at least one alkylene oxide having at least 3 carbon atoms, where the mixture has a maximum ethylene oxide content of 20% by weight, 30 based on the mixture, is added on.

If a mixture of ethylene oxide and at least one alkylene oxide having at least 3 carbon atoms is added on, the content of ethylene oxide should be at least 0.5% by weight, based on the 35 mixture.

As alkylene oxides having at least 3 carbon atoms in the molecule, preference is given to using propylene oxide, butylene oxide and isobutylene oxide and also any mixtures of at least two 40 of the alkylene oxides mentioned, particularly preferably propylene oxide.

In a preferred embodiment of the present invention, ethylene oxide can be added onto the polyether alcohol at the end of the 45 chain, i.e. after the molecular addition of the alkylene oxides having at least 3 carbon atoms or of the mixture of ethylene oxide and alkylene oxides having at least 3 carbon atoms. The

amount of this ethylene oxide added onto the end of the chain is preferably not more than 15% by weight, based on the weight of the polyether alcohol. Such polyether alcohols are preferably used for producing cold-cure polyurethane foams. Polyether alcohols of the present invention without this ethylene oxide end block are preferably used for producing flexible polyurethane foams, in particular flexible slabstock foams.

It has surprisingly been found that the hydrophilicity of the
10 polyether alcohols of the present invention is significantly
lower than that of conventional polyether alcohols containing the
same amount of ethylene oxide in the polyether chain but having a
different distribution of alkylene oxides in the chain.

15 The present invention further provides a process for preparing the above-described polyether alcohols. The polyether alcohols of the present invention are prepared by ring-opening polymerization of the alkylene oxides ethylene oxide and the alkylene oxides having at least 3 carbon atoms onto H-functional initiator substances in the presence of catalysts.

In a preferred embodiment of the process of the present invention, the molecular addition of the total amount of alkylene oxide is carried out in the presence of basic catalysts. Basic catalysts which can be used are, for example, amines, basic salts, metal oxides and metal hydroxides. Preference is given to using alkali metal and/or alkaline earth metal hydroxides. In industry, potassium hydroxide is usually used.

30 In a further preferred embodiment of the process of the present invention, multimetal cyanides, frequently also referred to as DMC catalysts, are used as catalyst for the molecular addition of the alkylene oxides. The advantages of using these catalysts are firstly the higher reaction rate in the molecular addition of the alkylene oxides and secondly the fact that the polyether alcohols prepared in this way have a lower content of unsaturated constituents. However, this embodiment has the disadvantage that there can be a delayed start of the reaction at the beginning when using DMC catalysts.

In further preferred embodiments of the process of the present invention, the various sections of the polyether chain are added on using different catalysts. Thus, it is advantageous to add on an ethylene oxide block at the beginning of the chain using basic catalysts and to add on the subsequent block consisting entirely or predominantly of alkylene oxides having at least 3 carbon atoms using DMC catalysts. The ethylene oxide block which may, if

desired, be present at the end of the chain can likewise be added on by means of DMC catalysts, but preferably by means of basic catalysts. This procedure has the advantage that the delay which frequently occurs at the start of the reaction when using 5 multimetal cyanide catalysts is avoided. This is balanced by increased costs due to the additional purification step.

When using different catalysts, it may be necessary to purify the polyether alcohol to remove catalyst prior to changing the

10 catalysts. Particularly when changing from basic catalysts to DMC catalysts, a thorough purification is usually carried out because traces of the basic catalyst, in particular the alkali metal hydroxides customarily used, can poison the DMC catalyst.

15 The invention further provides polyurethanes which can be produced by reacting polyisocyanates with compounds having at least two hydrogen atoms which are reactive toward isocyanate groups, wherein the polyether alcohols of the present invention are used as compounds having at least two hydrogen atoms which
20 are reactive toward isocyanate groups. The polyether alcohols of the present invention are preferably used for producing flexible polyurethane foams, with the polyether alcohols without a terminal ethylene oxide block being used, in particular, for producing slabstock foams and hot-cure molded foams and the
25 polyether alcohols having a terminal ethylene oxide block being used, in particular, for producing cold-cure molded foams.

As initiator substances for preparing the polyetherols of the present invention, use is made of the customary polyfunctional 30 alcohols having from 2 to 8 hydroxyl groups in the molecule. In particular, 2- and/or 3-functional alcohols, for example ethylene glycol, propylene glycol, glycerol or trimethylolpropane, are used for preparing polyether alcohols as are customarily used for producing flexible polyurethane foams.

35

The polyether alcohols of the present invention preferably have a molecular weight in the range from 1000 to 100,000.

Alkylene oxides used are, as indicated above, ethylene oxide and 40 alkylene oxides having at least 3 carbon atoms, in the abovementioned ratios.

The multimetal cyanides used as catalysts in the process of the present invention usually have the formula (I)

45

 $M_a^1[M^2(CN)_b(A)_c]_d \cdot fM^1gX_n \cdot h(H2O) \cdot eL (I)$,

where

- M¹ is a metal ion selected from the group consisting of Zn^{2+} , Fe^{2+} , Co^{3+} , Ni^{2+} , Mn^{2+} , Co^{2+} , Sn^{2+} , Pb^{2+} , Mo^{4+} , Mo^{6+} , Al^{3+} , V^{4+} , V^{5+} , Sr^{2+} , W^{4+} , W^{6+} , Cr^{2+} , Cr^{3+} , Cd^{2+} ,
 - $\rm M^2$ is a metal ion selected from the group consisting of Fe²⁺, Fe³⁺, Co²⁺, Co³⁺, Mn²⁺, Mn³⁺, V⁴⁺, V⁵⁺, Cr²⁺, Cr³⁺, Rh³⁺, Ru²⁺, Tr³⁺

10

and M^1 and M^2 are identical or different,

- A is an anion selected from the group consisting of halide, hydroxide, sulfate, carbonate, cyanide, thiocyanate, isocyanate, cyanate, carboxylate, oxalate and nitrate,
- x is an anion selected from the group consisting of halide, hydroxide, sulfate, carbonate, cyanide, thiocyanate, isocyanate, cyanate, carboxylate, oxalate and nitrate,

20

15

L is a water-miscible ligand selected from the group consisting of alcohols, aldehydes, ketones, ethers, polyethers, esters, ureas, amides, nitriles and sulfides,

25 and

a, b, c, d, g and n are selected so that the compound is electrically neutral, and

30

- e is the coordination number of the ligand,
- f is a fraction or integer greater than or equal to 0 and
- 35 h is a fraction or integer greater than or equal to 0.

These compounds are prepared by generally known methods by combining the aqueous solution of a water-soluble metal salt with the aqueous solution of a hexacyanometalate compound, in 40 particular a salt or an acid, and adding a water-soluble ligand

40 particular a salt or an acid, and adding a water-soluble ligand thereto during or after the mixing of the solutions.

Owing to their high activity, the multimetal cyanide compounds are very well suited to the synthesis of the polyether alcohols 45 of the present invention. The catalyst concentrations used are less than 1% by weight, preferably less than 0.5% by weight, particularly preferably less than 1000 ppm, in particular less

than 500 ppm, very particularly preferably less than 100 ppm, based on the total mass of the polyether polyol prepared. The preparation of the polyether alcohols by means of the multimetal cyanide compounds can be carried out either continuously or batchwise. The synthesis can be carried out in suspension, in a fixed bed, in a moving bed or in a fluidized bed.

As far as the reaction conditions pressure and temperature are concerned, there is no difference in principle between catalysis 10 by means of basic compounds and by means of multimetal cyanide compounds. The molecular addition of the alkylene oxides is carried out at from 50°C to 200°C, preferably from 90°C to 150°C, and at pressures in the range from 0.001 bar to 100 bar, preferably from 0.001 bar to 20 bar for the molecular addition of alkylene oxides having at least 3 carbon atoms in the molecule and preferably from 1 to 40 bar for the molecular addition of ethylene oxide. Before introducing the alkylene oxides, the reaction vessel is usually made inert by flushing with an inert gas, for example nitrogen.

The molecular addition of the alkylene oxides is usually followed by an after-reaction phase in order to effect complete reaction of the alkylene oxides.

25 After the reaction, the polyether alcohol formed is worked up in a customary fashion by firstly removing unreacted alkylene oxide and other volatile constituents from the crude polyether alcohol by stripping or distillation and, if necessary, removing suspended material and/or mechanical contamination by means of 30 filtration.

If the last process step was base-catalyzed, the catalyst has to be removed as usual from the polyether alcohol. For this purpose, the basic catalyst is usually neutralized with an acid and the salts formed are removed from the polyether alcohol by means of filtration.

If the last process step has been catalyzed using multimetal cyanide compounds, the catalyst can in principle remain in the 40 polyether alcohol, but it can also be removed if necessary, for example by means of filtration.

The polyether alcohols of the present invention are very well suited to the production of polyurethanes, in particular flexible 45 polyurethane foams. They are very readily compatible with the other constituents of the polyurethane formulations and have, despite their comparatively high content of ethylene oxide units

in the polyether chain, a low hydrophilicity. Owing to the higher reaction rate of the polymerization of ethylene oxide compared to propylene oxide, the space-time yield in the preparation of the polyether alcohols of the present invention is higher than that

- 5 in the case of conventional polyether alcohols for the same application areas. A further increase in the space-time yield can be achieved when at least part of the alkylene oxides is added on using multimetal cyanide compounds as catalyst.
- 10 The invention is illustrated by the following examples:

Examples 1 and 2

Addition of ethylene oxide onto an initiator substance

Example 1

1115 g of glycerol and 32.5 g of a 47% strength aqueous potassium hydroxide solution were placed in a 10 l reactor. The water was 20 removed at 95-100°C under a reduced pressure of less than 1 mm of mercury over a period of 1.5 hours. At 110°C and a nitrogen prepressure of 3.5 bar abs., 3980 g of ethylene oxide were metered in over a period of 6 hours. After reaction was complete, a water pump vacuum was applied, 250 g of Ambosol® magnesium 25 silicate and 50 g of water were subsequently added to remove the catalyst and the polyether alcohol was subsequently filtered and dewatered by means of distillation.

The polyether alcohol formed had the following properties: 30 hydroxyl number: 394 mg KOH/g, viscosity at 25°C: 240 mPa*s, potassium content: 5 ppm.

Example 2

35 The procedure of Example 1 was repeated, but 612 g of glycerol, 31.7 g of a 47% strength aqueous potassium hydroxide solution and 4356 g of ethylene oxide were reacted.

The polyether alcohol formed had the following properties: 40 hydroxyl number: 219 mg KOH/g, viscosity at 25 °C: 222 mPa*s, potassium content: 3 ppm.

Examples 3 and 4

Preparation of the polyether alcohols

5 The syntheses were carried out in a 10 l stirred reactor. This was charged with the reaction products from Examples 1 and 2 at 50°C. The contents of the reactor were made inert by evacuating three times and each time filling with nitrogen. Degassing was carried out by evacuation at 105°C and a pressure of less than 10 l mbar abs. for 1.5 hours. A double metal cyanide catalyst from the reaction of zinc acetate with hexacyanocobaltic acid and tert-butanol were then added. The reactor was again evacuated three times and each time filled with nitrogen. This was followed by evacuation to a pressure of less than 1 mbar abs. for about 15 half an hour with the temperature being increased to 125°C. At this temperature, a mixture of propylene oxide and ethylene oxide was added. After a further 30 minutes at 125°C, the polyether alcohol formed was freed of volatile constituents under reduced pressure. To remove the catalyst, the polyether alcohol was 20 filtered through a double layer of a Seitz deep filter (K 900).

The amounts of starting materials used and the properties of the polyether alcohols prepared are shown in Table 1.

25 Result:

All polyether alcohols have an inner block of glycerol and ethylene oxide. In Example 3, this is adjoined by a mixed block of ethylene oxide and propylene oxide, in Example 4 by a block of 30 propylene oxide.

Polyether alcohols which have only a small proportion of unsaturated constituents were obtained. Products having a very low hydroxyl number can also be obtained by the process of the present invention. The polyether alcohols have narrow molecular weight distributions in all cases.

Amounts of starting materials used and analyses of the polyether alcohols prepared Table 1

| Exam- | Polyether A | mount of | Catalyst | Propyle- | Ethylene | Catalyst Propyle- Ethylene Hydroxyl | Viscosity at Mn | | Mw | Unsaturated |
|-------|-------------|-----------|----------|----------------|----------|-------------------------------------|-------------------|------|------|------------------|
| ple | from | polyether | [6] | ne oxide oxide | oxide | number | 25 °C [mPa*s] [g] | | [6] | constituents |
| | Example | [6] | | [6] | [6] | [mgKOH/g] | | | | [med/g] |
| 3 | 1 | 7.609 | 2.141 | 4288 | 107 | 47.1 | 722 | 2877 | 3093 | 2877 3093 0.0066 |
| 4 | 2 | 1097.3 | 2.142 | 3909 | ı | 46.3 | 725 | 2849 | 3004 | 2849 3004 0.0058 |

Examples 5 (comparative example) and 6

Production of foams

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In Comparative Example 5 and Example 6, the polyol and isocyanate components shown in Table 2 were reacted to produce flexible polyurethane foams. The constituents of the polyol component were intensively mixed. The isocyanate component was then added while stirring and the reaction mixture was poured into an open mold in which it foamed to form the polyurethane foam.

The product properties of the polyurethane foam of the present invention are likewise summarized in Table 2. The testing 15 standards used are shown in Table 3.

Table 2: Production and properties of flexible slabstock foams

| 20 | | | Example 5 (C) | Example 6 |
|----|-----------------------|---------------------------------|---------------|------------|
| 25 | Polyol component | Hydroxyl number [mgKOH/g] | Amount [g] | Amount [g] |
| 23 | Polyol A | 48 | 1000 | |
| | Polyol from Example 4 | 48 | | 1000 |
| | Water | 6233 | 38 | 38 |
| 30 | BF 2370 | | 10 | 10 |
| | Amine catalyst N 201 | 560 | 1,9 | 1.9 |
| | Amine catalyst N 206 | 426 | 0.6 | 0.6 |
| | Tin catalyst K 29 | 0 | 2.3 | 2.5 |
| 35 | Total | | 1053 | 1053.0 |
| | Isocyanate component | NCO [%] | Amount [g] | Amount [g] |
| | TDI 80/20 | 48.3 | 488.0 | 488.0 |
| 40 | Index | | 110 | 110 |
| 40 | Test data | Unit | | |
| | Cream time | [s] | 15 | 10 |
| | Fiber time | [s] | 90 | 80 |
| 45 | Rise time | [s] | 90 | 85 |
| | Rise height | [mm] | 275 | 265 |

| | Rise height after 5 min | [mm] | 270 | 260 |
|----|---|----------------------|------|------|
| | Air permeability | [mmWs] | 10 | 10 |
| | Foam density | [kg/m ³] | 25.3 | 26.4 |
| 5 | Compressive strength at 40% compression | [kPa] | 4.7 | 4.1 |
| | Tensile strength | [kPa] | 79,1 | 88 |
| | Elongation | [%] | 121 | 146 |
| 10 | Compressive set at 50% compression | [%] | 2.4 | 2.4 |

Polyol A: Glycerol-initiated polyether alcohol having an inner block of 30 parts by weight of propylene oxide and an adjoining mixed block of 57 parts by weight of propylene oxide and 10 parts by weight of ethylene oxide.

Table 3: Testing standards

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| 20 | Test method | Standard |
|----|---|-----------|
| | Foam density | DIN 53420 |
| | Tensile test (tensile strength, elongation) | DIN 53571 |
| 25 | Compressive set | DIN 53572 |
| | Rebound resilience | DIN 53573 |
| | Indentation hardness | DIN 53576 |
| | Compressive strength | DIN 53577 |

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We claim:

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- A polyether alcohol which can be prepared by ring-opening 5 polymerization of ethylene oxide and at least one alkylene oxide having at least three carbon atoms in the molecule onto H-functional initiator substances, wherein ethylene oxide or a mixture of ethylene oxide and at least one alkylene oxide having at least three carbon atoms in the molecule, where the 10 mixture has an ethylene oxide content of at least 98% by weight, based on the mixture, is added, in each case in an amount of not more than 40% by weight, based on the weight of the polyether alcohol, onto the initiator substance and subsequently at least one alkylene oxide having at least 15 three carbon atoms in the molecule or a mixture of ethylene oxide and at least one alkylene oxide having at least three carbon atoms in the molecule, where the mixture has a maximum ethylene oxide content of 20% by weight, based on the mixture, is added on, and at least one multimetal cyanide 20 compound is used as catalyst.
 - 2. A polyether alcohol as claimed in claim 1, wherein propylene oxide, butylene oxide, isobutylene oxide or any mixtures of at least two of the alkylene oxides mentioned are used as alkylene oxides having at least three carbon atoms in the molecule.
- A polyether alcohol as claimed in claim 1, wherein propylene oxide is used as alkylene oxide having at least three carbon atoms in the molecule.
 - 4. A polyether alcohol as claimed in claim 1, wherein ethylene oxide is added on at the end of the chain.
- 35 5. A polyether alcohol as claimed in claim 4, wherein a maximum of 15% by weight of ethylene oxide, based on the weight of the polyether alcohol, is added on at the end of the chain.
- 6. A process for preparing polyether alcohols by ring-opening polymerization of ethylene oxide and at least one alkylene oxide having at least three carbon atoms in the molecule onto H-functional initiator substances, which comprises adding ethylene oxide or a mixture of ethylene oxide and at least one alkylene oxide having at least three carbon atoms in the molecule, where the mixture has an ethylene oxide content of at least 98% by weight, based on the mixture, in each case in an amount of not more than 40% by weight, based on the weight

of the polyether alcohol, onto the initiator substance and subsequently adding on at least one alkylene oxide having at least 3 carbon atoms in the molecule or a mixture of ethylene oxide and at least one alkylene oxide having at least 3 carbon atoms in the molecule, where the mixture has a maximum ethylene oxide content of 20% by weight, based on the mixture, and at least one multimetal cyanide compound is used as catalyst.

- 10 7. A process as claimed in claim 6, wherein at least one basic compound is used as catalyst for the addition of the ethylene oxide or of the mixture of ethylene oxide and at least one alkylene oxide having at least 3 carbon atoms in the molecule, where the mixture has an ethylene oxide content of 15 at least 98% by weight, based on the mixture, onto the initiator substance, and at least one multimetal cyanide compound is used as catalyst for adding on the alkylene oxide or oxides having at least 3 carbon atoms in the molecule or the mixture of ethylene oxide and at least one alkylene oxide 20 having at least 3 carbon atoms in the molecule, where the mixture has a maximum ethylene oxide content of 20% by weight, based on the mixture.
- 8. A process for preparing polyether alcohols as claimed in 25 claim 4, wherein at least one basic compound is used as catalyst for the addition of the ethylene oxide or of the mixture of ethylene oxide and at least one alkylene oxide having at least 3 carbon atoms in the molecule, where the mixture has an ethylene oxide content of at least 98% by weight, based on the mixture, onto the initiator substance 30 and at least one multimetal cyanide compound is used as catalyst for adding on the alkylene oxide or oxides having at least 3 carbon atoms in the molecule or the mixture of ethylene oxide and at least one alkylene oxide having at 35 least 3 carbon atoms in the molecule, where the mixture has a maximum ethylene oxide content of 20% by weight, based on the mixture, and at least one basic compound is used as catalyst for adding on the ethylene oxide at the end of the chain.
- 40 9. A polyurethane which can be produced by reacting polyisocyanates with compounds having at least two hydrogen atoms which are reactive toward isocyanate groups, wherein a polyether alcohol as claimed in any of claims 1 to 5 is used as compound having at least two hydrogen atoms which are reactive toward isocyanate groups.

Preparation of flexible slabstock foam polyols

Abstract

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Polyether alcohols can be prepared by ring-opening polymerization of ethylene oxide and at least one alkylene oxide having at least three carbon atoms in the molecule onto H-functional initiator substances, wherein ethylene oxide or a mixture of ethylene oxide and at least one alkylene oxide having at least three carbon atoms in the molecule, where the mixture has an ethylene oxide content of at least 98% by weight, based on the mixture, is added, in each case in an amount of not more than 40% by weight, based on the weight of the polyether alcohol, onto the initiator substance and subsequently at least one alkylene oxide having at least three carbon atoms in the molecule or a mixture of ethylene oxide and at least one alkylene oxide having at least three carbon atoms in the molecule, where the mixture has a maximum ethylene oxide content of 20% by weight, based on the mixture, is added on.

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0050/050735

DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

INVENTORSHIP IDENTIFICATION

My residence, post office address and citizenship are as stated below next to my name, I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

PREPARATION OF FLEXIBLE SLABSTOCK FOAM POLYOLS

SPECIFICATION IDENTIFICATION

| the specification | of which | | | |
|-------------------|--------------|---------------------------------|-------------|------------------|
| [] | is attached | hereto. | | |
| [] | was filed or | 1 | as | |
| | Application | a Serial No. | | |
| | and was an | nended on | | (if applicable). |
| [x] | was filed a | s PCT international application | | |
| | Number _ | PCT/EP00/08640 | _ | |
| | on _ | September 5, 2000 | _ | |
| | and was an | nended under PCT Article 19 | | |
| | on | (if applicable) | | |

ACKNOWLEDGMENT OF REVIEW OF PAPERS AND DUTY OF CANDOR

I hereby state that I have reviewed and understand the contents of the above—identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information known by me to be material to the patentability of this application in accordance with Title 37, Code of the Federal Regulations. \$1.56(a).

- [] In compliance with this duty there is attached an information disclosure statement. 37 CFR 1.97.
- [x] In compliance with this duty, information which may be material is disclosed in the specification of the subject application.

Page 2

0050/050735

CLAIM FOR BENEFIT OF EARLIER U. S. / PCT APPLICATION(S) UNDER 35 U. S. C. 120

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that / those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application(s) and the national of PCT international filing date of this application.

U. S. Application(s) (or PCT applications designating U. S.)

U. S. Application Serial No. Filing Date Status (pending, patented, abandoned)

RELATED FOREIGN APPLICATIONS

Related foreign applications, if any, filed in the name of the inventor(s) or the inventor(s) assigns more than twelve months before the filing of the subject application are as follows

Country Application No. Date of filing Date of issue or publication

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Page 3

0050/050735

POWER OF ATTORNEY

I hereby appoint the following attorney(s) and agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected herewith:

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CLAIM FOR BENEFIT OF FOREIGN PRIORITY UNDER 35 U.S.C. §119

Ihereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United State of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed.

- [] No such applications have been filed.
- [x] Such applications have been filed as follows

DETAILS OF FOREIGN APPLICATION FROM WHICH PRIORITY CLAIMED UNDER 35 U. S. C. §119

| Country Application No. Dat | te of filing D | ate of issue or | publication |
|-----------------------------|----------------|-----------------|-------------|
|-----------------------------|----------------|-----------------|-------------|

Germany 19944762.4 17 September 1999

Page 4

0050/050735

DECLARATION

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon

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0050/050735

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PATENT

(Docket No. 12122)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of

GEORG HEINRICH GROSCH et al.

Serial No.: NEW

Filed: HEREWITH

For: PREPARATION OF FLEXIBLE

SLABSTOCK FOAM POLYOLS

Group Art Unit: NEW

Examiner: Not Yet Assigned

I hereby certify that the attached correspondence is being deposited with the United States Postal Service in an envelope as Express Mail addressed to Commissioner of Patents and

Trademarks, Washington, D.C. 20231, on

ASSOCIATE POWER OF ATTORNEY (37 C.F.R. §1.34)

Hon. Commissioner of Patents and Trademarks Washington, D.C.

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